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Nonequilibrium Sorption during Displacement of Hydrophobic Organic Chemicals and (45)Ca through Soil Columns with Aqueous and Mixed Solvents

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16. ABSTRACT

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Nonequilibrium Sorption during Displacement of Hydrophobic Organic Chemicals and ^{45}Ca through Soil Columns with Aqueous and Mixed Solvents

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■ A series of miscible displacement experiments was conducted to investigate the significance of intraorganic matter diffusion (IOMD) as the rate-limiting step in sorption of organic and inorganic solutes during steady water flow in soil columns. Displacement studies were performed using Eustis surface soil and the same soil treated with hydrogen peroxide to reduce soil organic carbon content from 0.2% to <0.01%. Two herbicides (diuron and atrazine) were also displaced with binary solvent mixtures containing varying fractions of methanol and water (0–50% methanol). A bicontinuum nonequilibrium sorption model was used to simulate the measured effluent breakthrough curves (BTCs) obtained by simultaneous displacement of a nonadsorbed tracer (tritiated water), an organic solute (herbicide), and a metal cation (^{45}Ca). Support for IOMD as the rate-limiting step in sorption was provided by the following: (i) lack of asymmetry for the BTCs of tritiated water and ^{45}Ca in contrast to the asymmetrical BTCs of the two herbicides for aqueous displacements; (ii) symmetrical BTCs for all solutes displaced through the soil that was treated to remove organic matter; (iii) decreasing asymmetry with increasing methanol content in the displacing solution. An analysis of the bicontinuum sorption model parameters also supported this conclusion.

Introduction

Several mathematical models have been developed to predict transport of organic and inorganic contaminants through the vadose zone and in groundwater. Many of these models are based on the local equilibrium assumption (LEA). However, the validity of the LEA has recently become a topic of much interest, and methods have been proposed (*1–5*) to assess the applicability of the LEA model and the conditions under which it may be valid. Most of these efforts have involved the evaluation of the relative impacts of nonequilibrium sorption on solute transport and on the development of nonequilibrium criteria based on these impacts. To elucidate conditions under which nonequilibrium sorption may be important, the causative processes need to be investigated. Once these processes have been identified and studied, the ability to determine when the LEA is valid will be greatly enhanced. Information obtained from investigating nonequilibrium sorption is also essential for developing models that explicitly consider sorption kinetics. Such models are required to better predict organic contaminant transport under conditions of nonequilibrium sorption.

The occurrence, causes, and effects of nonequilibrium sorption were reviewed by Brusseau and Rao (*6*). They concluded that physical nonequilibrium (e.g., intraaggregate diffusion) and sorbate diffusion within the matrix of sorbent organic matter (intraorganic matter diffusion or IOMD) are the predominant rate-limiting mechanisms for the sorption of hydrophobic organic chemicals (HOCs). While physical nonequilibrium has been studied extensively (e.g., *7–16*), intraorganic matter diffusion has only recently begun to receive attention (cf. ref 17–22).

The conceptualization upon which IOMD is based requires that the sorbent organic matter has a three-dimensional structure. Organic matter in soils and sediments is commonly pictured as a three-dimensional network of polymer chains with a relatively open, flexible structure perforated with "voids" (*23–27*). A substantial amount of indirect evidence supporting the existence of an IOMD process has been presented (*6*, *17–22*). Diffusion within the organic matter matrix has been proposed by several researchers as a possible cause for nonequilibrium sorption of HOCs (*17–22*, *28–34*).

Evidence supporting the existence of IOMD, *albeit* indirect, is very strong (*22*). Experiments explicitly designed to investigate this process are now required. Direct, molecular-scale investigations of sorbate interactions with sorbent organic matter are preferred; however, such techniques are in the early stages of development. Hence, until such techniques are forthcoming, well-designed indirect experiments are necessary.

The purpose of this work was to appraise the contribution of IOMD to the nonequilibrium sorption existent during the displacement of two herbicides (diuron and atrazine) and a metal cation (^{45}Ca) through columns packed with a sandy soil (Eustis). A series of miscible displacement experiments was specifically designed to examine the influence of the sorption mechanisms and the role of soil organic matter in causing the observed nonequilibrium. The data for ^{45}Ca and the two herbicides were

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Table I. Properties of Eustis Soil

texture	fine sand
sand, %	93.8
silt, %	3.0
clay, %	3.2
organic carbon, %	0.2
pH (0.1 N $CaCl_2$)	5.7

Table II. Properties of Chemicals[a]

	MW	solub, mg/L	log K_{ow}	mp, °C	vp, mPa
atrazine	215.7	30 (20 °C)	2.32	175–177	40 (20 °C)
diuron	233.1	42 (25 °C)	2.81	158–159	412 (50 °C)

[a] solub, solubility in water; MW, molecular weight; mp, melting point; vp, vapor pressure.

utilized to explore the impact of the sorption mechanism (hydrophobic sorption versus isotopic exchange) on nonequilibrium sorption. Experimental approaches employed to investigate the role of soil organic matter involved perturbation of the solute–sorbent interactions, either by reducing the sorbent organic carbon (OC) content with H_2O_2 treatment or by increasing the sorbate solubility via addition of a miscible cosolvent (methanol). The effects of these perturbations upon the breakthrough curves (BTCs) of the organic solutes and of the inorganic cation were evaluated to discern the presence of IOMD. The BTCs of the sorbing solutes were contrasted with those of a nonadsorbed tracer (tritiated water) to demonstrate the absence of physical nonequilibrium. The measured BTCs were simulated with a bicontinuum sorption model to provide a quantitative basis for this analysis.

Experimental Section

Soil. Eustis soil Psammentic Paleudults was used as the sorbent for all experiments. This soil was selected because it has a relatively low organic carbon content (OC = 0.2%) and a low cation-exchange capacity (CEC). Organic matter is the predominant source for this CEC since the soil contained only 3% clay, with the major clay-size mineral being quartz. Chemical and physical properties of the Eustis soil are provided in Table I. Miscible displacement experiments were performed using both the untreated soil and soil that had been treated with hydrogen peroxide to reduce the OC content to less than 0.01%.

Sorbates. Two herbicides, diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], were employed as the HOCs. Although these herbicides have polar functional groups, both chemicals sorb to soil essentially as hydrophobic organic compounds (*35*). Selected properties of both pesticides are presented in Table II. Tritiated water was used as the conservative, nonsorbing tracer to evaluate the possible existence of physical nonequilibrium resulting from the presence of immobile-water regions in the soil column. Isotopic ion exchange was also investigated by studying the exchange between ^{40}Ca and ^{45}Ca following the method of Nkedi-Kizza et al. (*14*, *16*). Isotopic exchange was included in this study to examine the extent to which ion diffusion within the organic matter (which is the predominant source for CEC in this soil) may contribute to isotopic-exchange nonequilibrium.

Miscible Displacement. Air-dried Eustis soil was packed into preparative high-performance liquid chromatography (HPLC) glass columns (ALTEX; catalog no. 252-18), 2.5 cm in diameter and 30 cm in length. The bed length was adjusted to 5 cm. High-precision HPLC pumps were used to provide a steady flow rate. For each experiment, an electrolyte solution (0.01 N $CaCl_2$) containing three solutes (atrazine or diuron, ^{45}Ca, and tritiated water) was displaced through the soil columns. Column effluent fractions were collected after passage through a flow-through variable-wavelength UV detector (Waters Model 450). The activity of ^{45}Ca and tritiated water in the effluent fractions was measured by radioassay using liquid scintillation counting techniques for dual labeling (*36*). The herbicide concentration in the effluent was continuously monitored with the UV detector connected to a strip chart recorder (Linear; Model 1200). All displacements were performed under saturated, steady water flow conditions, at average pore-water velocities (v) of 5–6 cm/h. The influent concentrations for diuron and atrazine were 30 and 20 μg/mL, respectively. Further experimental details may be obtained from Nkedi-Kizza et al. (*18*).

Theory

Several models have been proposed for nonequilibrium sorption. Early attempts involved simple kinetic one-site sorption models (*37*, *38*); they generally provided poor simulations of experimental data. Currently, most nonequilibrium sorption models are based on a bicontinuum conceptualization. Two-region models, where the porous medium is divided into mobile and immobile regions, are often used to represent physical nonequilibrium. Models utilizing diffusion equations based on Fick's law have been proposed to describe mass transfer between the two regions (*13*, *14*, *39–42*). Use of these models requires knowledge of the geometric configuration of the immobile regions, which is often difficult to determine accurately. Hence, simpler models, wherein the mass transfer between the two regions is described with a first-order mass-transfer approximation, are more often employed. Coats and Smith (*43*) developed such a model for nonsorbing solutes and van Genuchten and Wierenga (*8*) extended it to sorbing solutes.

Bicontinuum models, often referred to as two-site models, have been used to represent chemical nonequilibrium sorption (*44*, *45*). These models assume the existence of two parallel classes of sorption sites: one class for which sorption at the sorbent–solvent interface is kinetically controlled, and another for which sorption is instantaneous. However, given the nature of hydrophobic partitioning (*46*, *47*), such conceptualization may not be valid for HOCs.

A bicontinuum approach may also be used to conceptualize sorbate mass transfer into the sorbent matrix (*34*, *48*). The two-site models discussed above, with the two classes of sites in series rather than in parallel, can be used to represent intraorganic matter diffusion (*6*). Lee et al. (*20*) and Brusseau et al. (*21*) employed the bicontinuum model to investigate nonequilibrium sorption of organic chemicals that was attributed to IOMD.

The two-region (first-order mass-transfer) and two-site models are mathematically equivalent for the case of linear sorption (*16*, *49*). The series and parallel conceptualizations of the two-site model are equivalent as long as equilibrium is assumed for one of the classes of sorption sites (*48*). Hence, the models used to represent the three nonequilibrium sorption processes are equivalent. As a result, the process(es) responsible for nonequilibrium sorption for a given case cannot be identified solely on the basis of curve-fitting the model(s) to experimental data.

The bicontinuum model may be conceptualized in the following manner:

$$C \leftrightarrow S_1 \rightleftarrows S_2 \qquad (1)$$

Table III. Model Parameter Values

expt no.	solute	parameter						conditions
		P	R	N	β	ω	P_{eff}	
1	^3H_2O	35	1.0					aqueous, normal soil
	^{45}Ca		4.60				20	aqueous, normal soil
	diuron	35	4.37	0.82	0.38	0.38		aqueous, normal soil
2	^3H_2O	53	1.0	1				aqueous, normal soil
	^{45}Ca		5.80				18	aqueous, normal soil
	atrazine	53	1.80	1	0.75	0.31		aqueous, normal soil
3	^3H_2O	180	1.0					aqueous, treated soil
	^{45}Ca		2.17				52	aqueous, treated soil
	diuron	180	1.18	1	0.90	1.54		aqueous, treated soil
4	^3H_2O	22	1.0					aqueous, treated soil
	^{45}Ca		2.27				15	aqueous, treated soil
	atrazine	22	1.10	1				aqueous, treated soil
5	^3H_2O	60	1.0					cosolvent, $f_c = 0.03$
	diuron	60	3.75	0.83	0.46	0.36		cosolvent, $f_c = 0.03$
	diuron	60	3.35	0.91	0.44	0.26		cosolvent, $f_c = 0.10$
	diuron	60	1.64	0.87	0.77	0.12		cosolvent, $f_c = 0.30$
	diuron	60	1.22	1.04				cosolvent, $f_c = 0.50$
6	^3H_2O	65	1.0					cosolvent, $f_c = 0$
	atrazine	65	1.80	1	0.73	0.29		cosolvent, $f_c = 0$
	atrazine	65	1.38	1	0.82	0.10		cosolvent, $f_c = 0.10$
	atrazine	65	1.16	1	0.93	0.07		cosolvent, $f_c = 0.30$
	atrazine	65	1.10	1				cosolvent, $f_c = 0.50$

where C is the solution-phase concentration [mass/length^3 (M/L^3)]; and S_1 and S_2 are the sorbed-phase concentrations (M/M) for the equilibrium and the kinetic domains, respectively. The distribution between the two types of sorption domains is described by F, defined as

$$F = K_{f1}/K_f \tag{2}$$

where K_{f1} and K_f $(ML^{-3})^{-N}$ represent the sorption coefficients for the type-1 domain and the entire sorbent, respectively. Hence,

$$S_T = (S_1 + S_2) = (K_{f1}C^N + K_{f2}C^N) = K_fC^N \tag{3}$$

where

$$S_1 = FK_fC^N \tag{4a}$$

$$S_2 = (1 - F)K_fC^N \tag{4b}$$

The bicontinuum sorption model coupled to the advective–dispersive (A–D) solute transport equation may be written in the dimensionless form

$$\frac{\partial C^*}{\partial p} + (\beta R - 1)NC^{*(N-1)}\frac{\partial C^*}{\partial p} + (1 - \beta)R\frac{\partial S^*}{\partial p} = \frac{1}{P}\frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \tag{5a}$$

$$(1 - \beta)R\frac{\partial S^*}{\partial p} = \omega(C^{*N} - S^*) \tag{5b}$$

by defining the following nondimensional parameters:

$$C^* = (C/C_0) \qquad P = (vL/D)$$

$$S^* = [S_2/(1 - F)K_fC_0^{N-1}]$$

$$R = [1 + (\rho/\theta)K_fC_0^{N-1}] \tag{6}$$

$$p = (vt/L) \qquad \beta = [1 + (\rho/\theta)FK_fC_0^{N-1}]/R$$

$$X = (x/L) \qquad \omega = [k(1 - \beta)RL/v]$$

where k is the first-order rate coefficient $(1/T)$, D is the dispersion coefficient (L^2/T), v is pore-water velocity (L/T), x is distance (L), L is column length (L), N is the Freundlich nonlinear sorption isotherm coefficient, ρ is bulk density (M/L^3), θ is volumetric water content (L^3/L^3), and C_0 is the influent solute concentration (M/L^3). Note that the Fruendlich model (eq 4) is used to represent equilibrium sorption isotherms. Thus, isotherm nonlinearity can be accounted for with this model. In most earlier dimensionless formulations of the two-site model (*16*, *45*), the sorption isotherms were restricted to the linear form.

Table IV. k and K_f Values

expt	conditions	k, h^{-1}	K, (mL/g)$^{-N}$
diuron	aqueous	0.15	1.44
diuron	methanol, $f_c = 0.03$	0.18	1.29
diuron	methanol, $f_c = 0.1$	0.14	0.84
diuron	methanol, $f_c = 0.3$	0.34	0.26
atrazine	aqueous, $f_c = 0$	0.77	0.15
atrazine	methanol, $f_c = 0.1$	0.50	0.07
atrazine	methanol, $f_c = 0.3$	0.67	0.03

Parameter Determination/Estimation. The solute transport equations (eq 5a and 5b) were solved under constant solute flux boundary conditions by a Crank–Nicholson finite-difference method. Parameters were determined by coupling the numerical solution to the transport model with a nonlinear least-squares (NLLS) optimization program UWHAUS (*50*).

The Peclet number (P) was determined by fitting the LEA model to the BTC of tritiated water. The value for the retardation factor (R) was calculated (see eq 6) by using the measured sorption isotherm parameters (K_f and N) and ρ and θ values for the columns. With the values of P and R fixed, the nonequilibrium sorption parameters (ω and β) for the sorbing solutes were optimized to obtain the best fit to the experimental data. Model parameter values for the various displacement studies are summarized in Tables III and IV.

Results and Discussion

Displacement with Aqueous Solutions. Tritiated water was employed as a nonadsorbed, conservative tracer to investigate the hydrodynamic character of the porous medium. The BTCs obtained from displacement of tritiated water through the Eustis soil columns are presented in Figures 1–6. The BTCs are symmetrical and sigmoidal in shape, suggesting the absence of physical nonequilibrium processes in the porous medium (*6*, *18*, *20*).

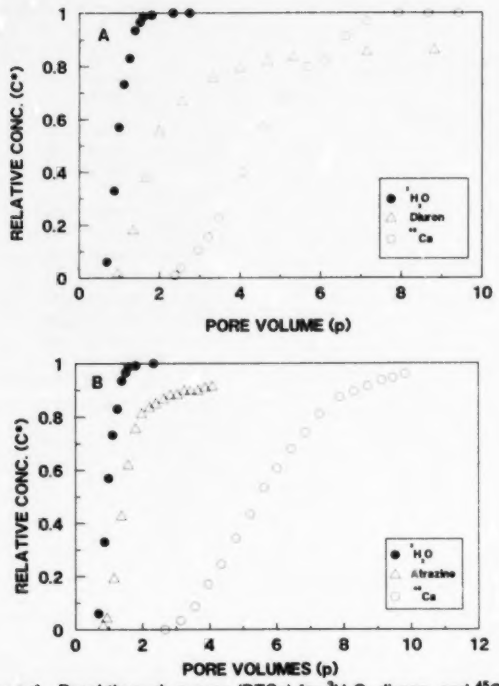

Figure 1. Breakthrough curves (BTCs) for ^3H_2O, diuron, and ^{45}Ca (A) and ^3H_2O, atrazine, and ^{45}Ca (B).

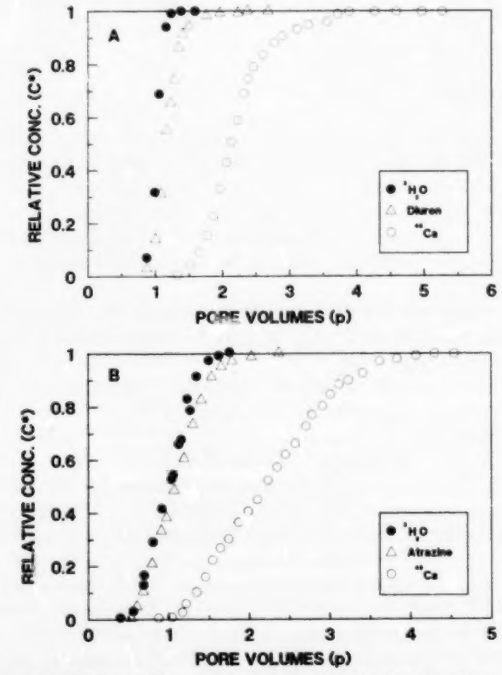

Figure 2. Similar to Figure 1 except the soil is H_2O_2-treated.

The BTCs obtained from a simultaneous displacement of diuron or atrazine, ^{45}Ca, and tritiated water through the soil columns (experiments 1 and 2) are presented in Figure 1. Note that, while the BTCs for tritiated water and ^{45}Ca are symmetrical and sigmoidal in shape, the BTCs for ^{45}Ca are rotated clockwise in comparison to the BTC for tritiated water; this suggests increased dispersion of ^{45}Ca. In contrast, the BTCs for both diuron and atrazine are asymmetrical, with pronounced tailing in approach to $C^* = 1$. Tailing or increased dispersion is typical for BTCs

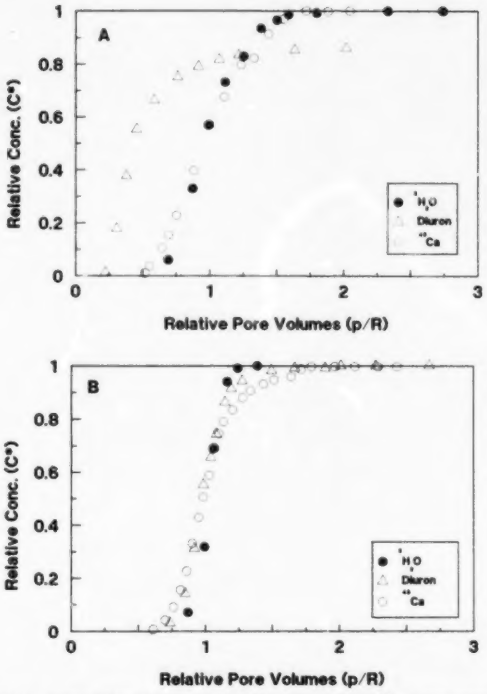

Figure 3. Normalized BTCs for ^3H_2O, diuron, and ^{45}Ca for untreated and H_2O_2-treated soil (A and B, respectively).

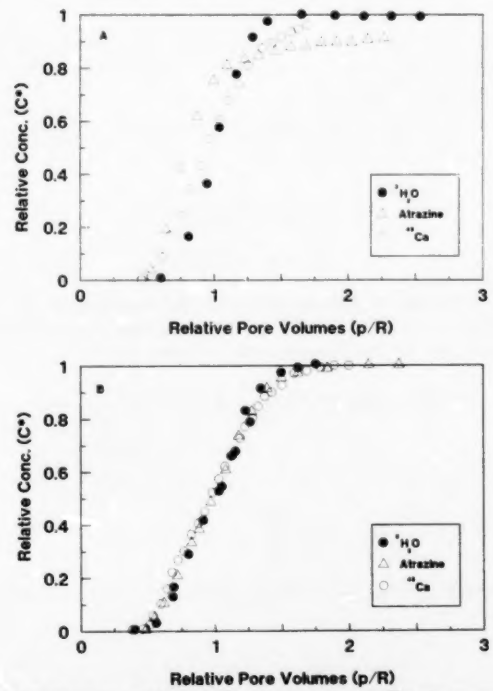

Figure 4. Normalized BTCs for ^3H_2O, atrazine, and ^{45}Ca for untreated and H_2O_2-treated soil (A and B, respectively).

obtained under nonequilibrium conditions (*6*). The fact that only the BTCs for the sorbing solutes exhibit increased dispersion or asymmetry suggests that the mechanism responsible for nonequilibrium is related to the sorption process.

To investigate the role of sorbent organic matter in nonequilibrium sorption, the solutes were displaced through columns packed with Eustis soil for which the OC

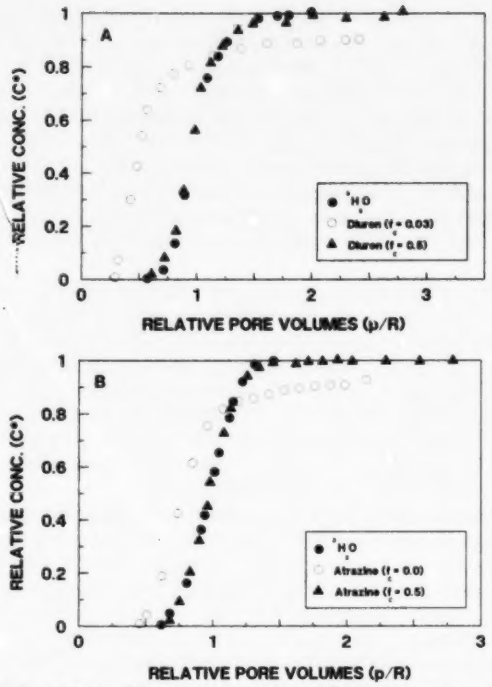

Figure 5. BTCs for ^3H_2O and diuron (A) and ^3H_2O and atrazine (B) in methanol–water mixtures.

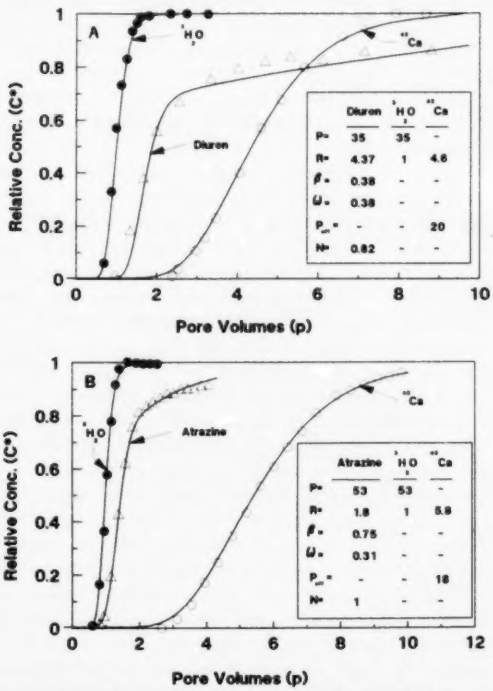

Figure 6. Observed and calculated (line) BTCs for ^3H_2O, diuron, and ^{45}Ca (A) and ^3H_2O, atrazine, and ^{45}Ca (B).

content was reduced to <0.01% by H_2O_2 treatment. The BTCs obtained from these displacements were symmetrical for all solutes (Figure 2, parts A and B). Atrazine sorption was reduced to essentially zero and there was also a considerable decrease in the retention of diuron and ^{45}Ca in these experiments (3 and 4) compared to those utilizing the untreated soil (experiments 1 and 2).

To facilitate evaluation of BTC asymmetry, the BTCs of sorbing solutes may be normalized for retardation and plotted along with the BTC for the conservative, nonadsorbed tracer. In such plots, the normalized BTCs will be coincident with that of the nonadsorbed solute when the sorbing solute is not influenced by nonideal-sorption processes (i.e., sorption-related nonequilibrium, sorption isotherm nonlinearity, etc.). The normalized BTCs will not be coincident, however, when such processes are operative.

The BTCs for diuron, atrazine, and ^{45}Ca were normalized by their respective retardation factor (R) values and are plotted along with the BTCs for tritiated water in Figures 3 and 4. The BTCs for the two herbicides are obviously not coincident with those of tritiated water (Figures 3A and 4A). Although the BTCs for ^{45}Ca are symmetrical, in contrast to those of the pesticides (Figures 3A and 4A), they are rotated clockwise in relation to the BTCs of tritiated water. This behavior suggests that, while both ^{45}Ca and the two herbicides are experiencing nonequilibrium sorption, the degree of nonequilibrium is much less for ^{45}Ca. In other words, the isotopic exchange of ^{45}Ca appears to have been near enough to equilibrium such that an increase in the dispersion was the only apparent impact of nonequilibrium. Under these conditions, the effective dispersion (ED) model can be used to account for the observed nonequilibrium (*6*, *20*).

The normalized BTCs for diuron, atrazine, and ^{45}Ca displacement through the columns packed with H_2O_2-treated soil are also plotted along with the BTCs of tritiated water in Figures 3B and 4B. The BTCs for the sorbed solutes are essentially coincident with those of tritiated water. Hence, it may be concluded that the nonequilibrium mechanism is associated with the sorbent organic matter.

Considering the differences in the degree of nonequilibrium exhibited by ^{45}Ca and the herbicides, the process by which ^{45}Ca is interacting with the organic matter is apparently much faster than that by which the herbicides are interacting. This could be a result of ^{45}Ca having a larger D_e or a smaller effective diffusive path length, or it could also be reflective of a different sorption mechanism. Several researchers have demonstrated that ion exchange is an instantaneous, physical stoichiometric process involving no chemical bond formation (e.g., ref 7 and 51). These results imply that ion diffusion to/from the exchanger, rather than the actual exchange "reaction" itself, is the rate-limiting step for ion exchange (*7*, *14*, *16*). In addition, based on the double layer theory, the electroneutrality requirements for ion exchange can be satisfied by ions residing within the electrical field of the sorbent; thus, the ions do not have to be at the exchanger surface. Furthermore, it is likely that a greater proportion of the charge sites associated with soil organic matter are located near the solution interface. For these reasons, it might be expected that the diffusion path length for ^{45}Ca would be shorter than that for diuron or atrazine, whose sorption mechanism is thought to involve diffusive mass transfer into the three-dimensional structure of organic matter.

Displacement with Mixed Solvents. Rate-limited interactions between the sorbate and the sorbent organic matter are apparently responsible for the nonequilibrium sorption observed in the experiments discussed above. The nature of these interactions was further investigated via the use of miscible cosolvents. Nkedi-Kizza et al. (*18*) presented BTCs obtained from miscible displacement of diuron and atrazine (in aqueous solutions with varying fractions of methanol) through columns packed with Eustis soil. They observed the degree of BTC asymmetry (i.e.,

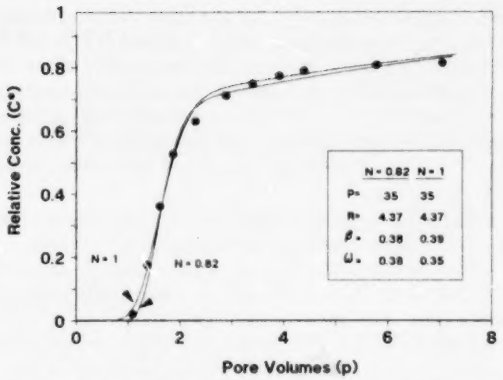

Figure 7. Observed and calculated (line) BTC for diuron. The IOMD model was used for a linear isotherm (N = 1) and for a nonlinear isotherm (N = 0.82).

nonequilibrium sorption) to decrease with increasing volume fraction (f_c) of cosolvent; this behavior was attributed to interactions between the solvent and sorbent organic matter. A similar effect of a reduction in the asymmetry of BTCs obtained from displacement of phenanthrene, naphthalene, and diuron through Eustis soil with increasing fraction of methanol was reported by Wood et al. (*52*).

To facilitate evaluation of the degree of asymmetry as influenced by variation in f_c, the BTCs obtained by Nkedi-Kizza et al. (*18*) were normalized by their R values (see Figure 5, parts A and B). It is apparent that the degree of divergence from the BTC of tritiated water decreases as f_c increases. When f_c = 0.5, the BTCs of the herbicides are essentially coincident with that of tritiated water.

Model Simulations. The fit of the advective–dispersive (A–D) model to the BTCs for tritiated water are shown in Figure 6, parts A and B. Dimensionless model parameter values for this and all other experiments are provided in Table III. As noted earlier, ^{45}Ca is near enough to equilibrium such that the ED model may be used. This model employs an effective Peclet number (P_{eff}) in place of the hydrodynamic dispersion coefficient in the A–D model. P_{eff} incorporates any dispersion resulting from nonequilibrium sorption as well as that from hydrodynamic dispersion (*6*, *13*, *20*). The fit of the ED model to the ^{45}Ca data, and the fit of the two-site model to the BTCs for diuron and atrazine, are shown in Figure 6.

The sorption isotherms for diuron were nonlinear, with N values ranging from 0.82 to 0.91 (see Table III). To investigate the impact of nonlinearity, the BTCs for diuron were simulated with N set equal to 1. An example (worst case) of the results of these simulations compared to the previous simulations (N set equal to the values shown in Table III) is shown in Figure 7. It is apparent that there is negligible difference between the simulations obtained for the BTC with a linear isotherm and those obtained with a nonlinear isotherm. The k values determined with N set equal to 1 differed by approximately 5% from those determined with a nonlinear sorption isotherm. This relative insignificance of nonlinearity in comparison to nonequilibrium sorption has also been observed by others (*10*, *53*, *54*). It should be recognized, however, that the distal limb of a BTC will be more sensitive to nonlinearity of the sorption isotherm than will the frontal limb (*6*).

Kinetic parameter values obtained by fitting the bicontinuum model to the BTCs for diuron and atrazine (in aqueous solution) are given in Tables III and IV. The first-order rate coefficient (k) for both diuron and atrazine is much larger for the experiments utilizing soil with reduced OC content. This inverse relationship between k and OC content has also been observed by others (*6*, *21*, *22*, *34*, *48*). Such a relationship is suggestive of an intraorganic matter diffusion process. For the IOMD model, k may be thought of as a lumped parameter incorporating characteristics of both the sorbent and the sorbate, including the effective diffusion coefficient and the diffusive path length. It is likely that treating the soil to reduce the sorbent OC content in effect reduces the mean diffusive path length, which results in an increase in the value of k.

To quantitatively evaluate the effect of miscible cosolvent addition upon nonequilibrium sorption, the two-site model was used to simulate the BTC data of Nkedi-Kizza et al. (*18*) for diuron and atrazine displacement with mixed solvents; optimized model parameter values are summarized in Tables III and IV. For diuron, the first-order rate coefficient, k, increased linearly (r^2 = 0.83) with volume fraction of the cosolvent (f_c). No such relationship was found (r^3 = 0.03) for the atrazine data.

A relationship between k and f_c is indicative of an intraorganic matter diffusion process. As discussed above, k incorporates among other components the effective diffusion coefficient (D_e). The effective diffusion coefficient, in turn, incorporates the diffusivity of the chemical, the effects of retardation upon this diffusivity, and the resistance to diffusion provided by the sorbent. The effect of miscible cosolvent addition is to increase D_e, which results in an increase in the value of k.

Addition of a water-miscible cosolvent may increase the effective diffusion coefficient in two ways: (a) the sorption partition coefficient has been shown to exponentially decrease with increasing f_c (*35*, *55–57*). A decrease in the partition coefficient would cause a decrease in retardation, which would result in a larger D_e; (b) the presence of the cosolvent may cause the sorbent organic matter to swell, which would result in a reduction in the resistance afforded by the organic matter to sorbate diffusion. However, as the organic matter swells, the effective path length for diffusion will increase, thus attenuating the effect of swelling on increasing the value of D_e. Swelling of sorbent organic matter was postulated by Freeman and Cheung (*17*) as being responsible for the decrease in time required for desorption (solvent extraction) that occurred with cosolvent addition. Walters and Guiseppie-Elie (*55*) have also observed a reduction in the time required to reach sorption equilibrium (in batch studies) with addition of miscible cosolvent. Considering that the partition coefficient decreases exponentially with increasing f_c, it is probable that (a) is the predominant factor influencing the change in D_e that occurs upon the addition of a cosolvent.

The first-order rate coefficient appears to exhibit an inverse relationship with the partition coefficient (Table III). This relationship has also been observed by other researchers (*22*, *34*, *48*). Such a relationship, especially in concert with the evidence presented earlier, suggests that diffusive mass transfer within the interior of sorbent organic matter was the process responsible for the nonequilibrium sorption observed during the displacement of diuron and atrazine through soil columns.

Summary and Conclusions

Diffusive mass transfer of sorbate within the matrix of sorbent organic matter is suggested as the mechanism responsible for the nonequilibrium sorption observed during the displacement of two herbicides (diuron and atrazine) and ^{45}Ca through a sandy soil. The following evidence supports this hypothesis: (1) only the BTCs of the sorbing solutes exhibited the effects of nonequilibrium,

suggesting that the nonequilibrium mechanism was sorption-related; (2) the BTCs of the sorbing solutes obtained from displacement through soil whose organic carbon content was significantly reduced exhibited no effects of nonequilibrium, suggesting that the nonequilibrium mechanism involved organic matter; (3) the BTCs of diuron and atrazine exhibited a decrease in asymmetry with increasing fractions of water-miscible organic solvent in the displacing solution, further supporting rate-limited interactions between sorbate and organic matter as being responsible for the nonequilibrium; and (4) the inverse relationships between k and K_f and between k and OC content, which suggest the involvement of a diffusive mass-transfer mechanism in the nonequilibrium sorption process.

Registry No. Methanol, 67-56-1; Diuron, 330-54-1; atrazine, 1912-24-9.

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